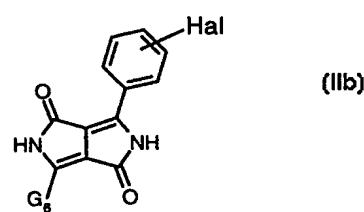
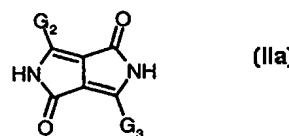
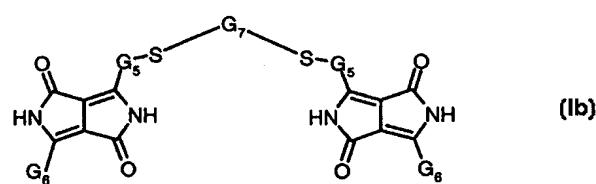
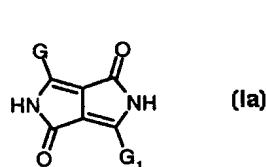


(51) International Patent Classification 6 : C07D 487/04, 519/00, A61K 31/40, C07B 45/06		A1	(11) International Publication Number: WO 99/54332 (43) International Publication Date: 28 October 1999 (28.10.99)
(21) International Application Number:	PCT/EP99/02513		
(22) International Filing Date:	14 April 1999 (14.04.99)		
(30) Priority Data:	915/98 22 April 1998 (22.04.98)	CH	
(71) Applicant:	CIBA SPECIALTY CHEMICALS HOLDING INC. [CH/CH]; Klybeckstrasse 141, CH-4057 Basel (CH).		
(72) Inventors:	HAO, Zhimin; Gstaltenrainweg 75, CH-4125 Riehen (CH). ROCHAT, Alain, Claude; Route de Schifffenen 40, CH-1700 Fribourg (CH). SCHLÖDER-TEBALDI, Nancy; Chemin des Glycines 6, CH-1753 Matran (CH).		

(54) Title: PREPARATION OF ALKYLTHIO- AND/OR ARYLTHIO-SUBSTITUTED DIKETO-DIARYL-PYRROLOPYRROLES



(57) Abstract

Preparation of alkylthio and/or arylthio-substituted diketo-diaryl-pyrrolopyrroles (DPPs) of formula (Ia) and dithio-bridged bis-diketo-diaryl-pyrrolopyrroles (bis-DPPs) of formula (Ib), in which in formula (Ia) G is phenyl substituted by at least one arylthio or alkylthio group, and G₁ is G or a carbocyclic or heterocyclic radical, by reacting a haloaryl with a thiol or thiolate, and in formula (Ib) G₅ is a phenylene, G₆ is G₁ but not G, and G₇ is alkylene, cycloalkylene or phenylene, by reacting two haloaryls with a dithiol or dithiolate, which comprises reacting a thiol or thiolate with a halo-diketo-diaryl-pyrrolopyrrole ("halo-DPP") of formula (IIa) in which G₂ is a halogenated phenyl group and G₃ is G₂ or G₁, or reacting a dithiol or dithiolate with two halo-diketo-diaryl-pyrrolopyrroles ("halo-DPPs") of formula (IIb) in which Hal is halogen such as fluorine, chlorine, bromine or iodine, and G₆ is G₁, and also novel DPPs and also bis-DPPs, compositions comprising DPPs of formula (Ia) prepared in accordance with the invention, and their uses.

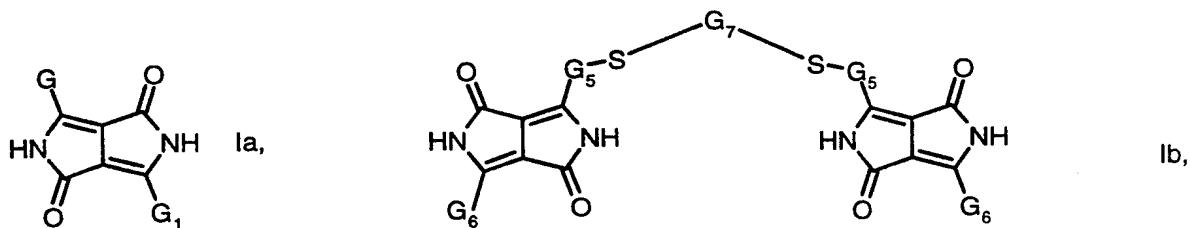
FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

Preparation of alkylthio- and/or arylthio-substituted diketo-diaryl-pyrrolopyrroles

The present invention relates to an improved process for preparing alkylthio- and/or arylthio-substituted diketo-diaryl-pyrrolopyrroles (DPPs) of the formula Ia and dithio-bridged bis-diketo-diaryl-pyrrolopyrroles (bis-DPPs) of the formula Ib



in which in formula Ia

G is phenyl substituted by at least one arylthio or alkylthio group, and

G₁ is G or a carbocyclic or heterocyclic radical, by reacting a haloaryl with a thiol or thiolate, and

in formula Ib

G₅ is a phenylene, G₆ is G₁ but not G, and G₇ is alkylene or phenylene, by reacting two haloaryls with a dithiol or dithiolate.

The invention additionally relates to novel, arylthio- or alkylthio-substituted DPPs, their use, and compositions comprising the DPPs of the invention.

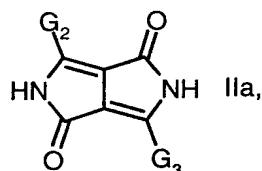
US 4,579,949 and US 4,490,542 describe the preparation of DPPs substituted by at least one thioether group by reacting arylthio- or alkylthio-substituted benzonitriles with succinic esters. Disadvantages are the low yields in the case of long-chain alkylthio-DPPs and the impossibility of obtaining water-soluble compounds.

The reaction of DPP pigments with thiols to give alkylthio- or arylthio-substituted DPPs gives incomplete conversions owing to the poor solubility of these pigments.

Chemistry Letters 1978, 13-14 discloses that unactivated haloaryls can be substituted only in the presence of catalysts.

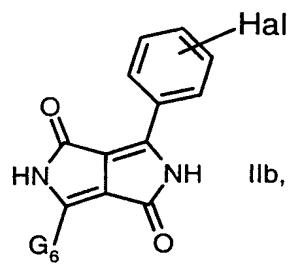
It was therefore an object of the invention to provide an improved process for preparing alkylthio- and/or arylthio-substituted DPPs which permits in particular the preparation of water-soluble compounds and long-chain alkylthio-DPPs. In particular, the process should be operable without high pressures and the use of catalysts. In addition, the economics of the process should be guaranteed by high yields. Furthermore, the invention was to provide novel, thioether-substituted diketo-diaryl-pyrrolopyrroles and also dithioether-bridged bis-DPPs which can be used in compositions with high molecular mass organic material, in particular as colorants. In addition, the thioether-substituted DPPs should be able to be used, in particular, as crystal growth inhibitors or rheology enhancers.

Accordingly, we have found the process defined at the outset, which involves reacting a thiol or thiolate with a halo-diketo-diaryl-pyrrolopyrrole ("halo-DPP") of the formula IIa



in which G₂ is an unsubstituted or substituted, halogenated phenyl group and G₃ is G₂ or G₁, or

reacting a dithiol or dithiolate with two halo-diketo-diaryl-pyrrolopyrroles ("halo-DPPs") of the formula IIb



in which Hal is halogen such as fluorine, chlorine, bromine or iodine, preferably chlorine or bromine and, with particular preference, chlorine,

Hal being, in particular, in the para position of the phenylene.

Customarily, the reaction is started by bringing the thiol and/or thiolate or the dithiol and/or the dithiolate into contact with the halo-DPP IIa or IIb by conventional methods, for example by mixing the starting materials or by dropwise addition of one starting material to the other.

To prepare the compounds of the formula Ia the molar ratio of thiol to halo-DPP of the formula IIa is generally chosen to be within the range from 0.1:1 to 20:1, preferably in the range from 2:1 to 5:1 and, with particular preference, in the range from 2.1:1 to 2.7:1, and, to prepare the compounds of the formula Ib, the molar ratio of dithiol to halo-DPP of the formula IIb is generally chosen to be in the range from 0.5:1 to 20:1, preferably in the range from 0.5:1 to 5:1 and, with particular preference, in the range from 1:1 to 2.7:1.

Preferably, the reaction temperature is chosen to be within the range from 323 to 453 K, preferably in the range from 333 to 433 K, with particular preference in the range from 343 to 423 K and, with very particular preference, in the range from 343 to 413 K.

The reaction pressure is chosen to be generally within the range from 70 kPa to 10 MPa, preferably from 90 kPa to 5 MPa; atmospheric pressure is particularly preferred.

The reaction time depends generally on the reactivity of the starting materials, the chosen reaction temperature and the desired conversion. The reaction time is customarily chosen to be within the range from 15 minutes to 2 days.

In one preferred embodiment the reaction is conducted under an inert gas atmosphere using for this purpose preferably nitrogen or noble gases such as helium or argon. Particular preference is given to reaction in a nitrogen atmosphere.

In addition, the reaction can be carried out with or without solvent, with preference being given to reaction in a solvent. Preferred solvents are organic solvents or solvent mixtures such as aprotic, especially non-aqueous aprotic, solvents. Aprotic solvents may be apolar, such as benzene, chlorobenzene and chlorinated hydrocarbons, or polar. The latter are particularly preferred. Examples of polar aprotic solvents which can be used are amides such as hexamethyl-phosphoramide, carboxamides such as N,N'-dimethylformamide and N,N'-dimethylacetamide, or lactams such as N-methylpyrrolidone, N-methyl-2-piperidone, 1,3-dimethyl-3,4,5,6-tetrahydro-3(1H)pyrimidinone or N-methyl-4-piperidone, or urea bases such as N,N'-dimethylethyleneurea, N,N'-dimethyl-propyleneurea, and also acetonitrile, sulfolane, dimethyl sulfoxide, or aromatic solvents such as nitrobenzene.

Preference is given to N,N'-dimethylformamide, N,N'-dimethylacetamide, dimethyl sulfoxide, 1,3-dimethyl-3,4,5,6-tetrahydro-3(1H)pyrimidinone or N-methyl-pyrrolidone.

The weight ratio of halo-DPP IIa or halo-DPP IIb to the solvent lies in general within the range from 0.5 to 10% by weight, with particular preference in the range from 1 to 5% by weight and, with very particular preference, in the range from 2 to 3% by weight.

In another preferred embodiment the reaction is conducted in the presence of a base. Examples of suitable bases are alkali metal carbonates, for example Na_2CO_3 or K_2CO_3 , alkali metal hydrogencarbonates, for example NaHCO_3 or KHCO_3 , alkali metal hydroxides, for example NaOH or KOH , alkali metals, such as sodium or potassium, and also aromatic bases, such as pyridine, N,N'-dimethylaminopyridine or quinoline. Preference is given to non-aqueous alkali metal bases and to aromatic bases, particular preference to non-aqueous alkali metal carbonates or alkali metal hydrogencarbonates, and very particular preference to anhydrous K_2CO_3 .

The molar ratio of base to thiol or thiolate lies customarily within the range from 0.5:1 to 5:1, preferably in the range from 1:1 to 4:1 and, with particular preference, in the range from 1:1 to 3:1, and the molar ratio of base to dithiol or dithiolate lies customarily within the range from 1:1 to 10:1, preferably within the range from 1:1 to 5:1 and, with particular preference, in the range from 1:1 to 4:1.

In a preferred embodiment of the process of the invention the reaction is conducted in the presence of a solvent or solvent mixture and a base.

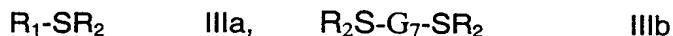
If desired, the reaction can also be conducted in the presence of catalysts, especially transition metal catalysts, examples being tetrakis(triphenylphosphine)palladium(0), -nickel(0), and -platinum(0), and -ruthenium(II) chloride. Preferably, the reaction is conducted without a catalyst.

If a catalyst is used, it is generally employed in a proportion within the range from 0.001 to 10% by weight, based on halo-DPP of the formula IIa or IIb, and preferably from 0.5 to 7% by weight and, with particular preference, from 2 to 5% by weight based on the total amount of reactants.

The reaction mixture can be worked up by conventional methods, for example by filtration and subsequent washing of the filter residue and subsequent optional drying. The product may be an individual compound or a mixture of differently substituted compounds of the formula Ia, or a mixture consisting of halo-DPP IIa and a compound of the formula Ia, or else a mixture consisting of halo-DPP IIb and a compound of the formula Ib and/or Ia.

In accordance with observations made to date the thiol or thiolate employed can comprise any known thiols or thiolates, examples being substituted or unsubstituted aryl or alkyl thiolates, it being possible for the latter to be branched or straight-chain, uninterrupted, or interrupted one or more times by heteroatoms.

In a preferred embodiment a thiol or thiolate of the formula IIIa or a dithiol or dithiolate of the formula IIIb is used.



in which

R_1 can be $\text{C}_1\text{-C}_{30}$ alkyl which can be uninterrupted or interrupted one or more times by heteroatoms, such as $-\text{O-}$ or $-\text{S-}$, or by $-\text{NH-}$, $-\text{C}(\text{O})\text{O-}$, $-\text{O-C}(\text{O})-$ or $-\text{C}(\text{O})\text{-NH-}$, and can be substituted or unsubstituted, or can be $\text{C}_5\text{-C}_{12}$ cycloalkyl or phenyl, each of which can be substituted or unsubstituted, and

R_2 is hydrogen, a cation ("M") of an alkali metal, or an organic nitrogen base, and G_7 can be $\text{C}_1\text{-C}_{30}$ alkylene which can be uninterrupted or interrupted one or more times by heteroatoms, such as $-\text{O-}$ or $-\text{S-}$, or by $-\text{NH-}$, $-\text{C}(\text{O})\text{O-}$, $-\text{O-C}(\text{O})-$ or $-\text{C}(\text{O})\text{-NH-}$, and can be substituted or unsubstituted, or

can be C₅-C₁₂cycloalkylene or phenylene, each of which can be substituted or unsubstituted.

C₁-C₃₀alkyl is methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, sec-amyl, tert-amyl, hexyl, 2,2-dimethylbutyl, heptyl, octyl, 2-ethylhexyl, 1,1',3,3'-tetramethylbutyl, nonyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl, eicosyl, heneicosyl, docosyl, tetracosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl or nonacosyl, preference being given to C₁-C₁₈alkyl such as methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, sec-amyl, tert-amyl, hexyl, 2,2-dimethylbutyl, heptyl, octyl, 2-ethylhexyl, 1,1',3,3'-tetramethylbutyl, nonyl, decyl, dodecyl, tetradecyl, hexadecyl and octadecyl

and particular preference to C₈-C₁₈alkyl such as octyl, 2-ethylhexyl, 1,1',3,3'-tetramethylbutyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl or octadecyl

and very particular preference to C₁₂-C₁₈alkyl such as dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl or octadecyl; particular preference is also given to C₁-C₈alkyl such as methyl, ethyl, propyl, isopropyl, n-butyl, iso-butyl, sec-butyl, tert-butyl, n-pentyl, sec-amyl, tert-amyl, hexyl, 2,2'-dimethylbutyl, heptyl, octyl, 2-ethylhexyl and 1,1',3,3'-tetramethylbutyl.

C₁-C₃₀alkylene is methylene, ethylene, propylene, isopropylene, n-butylene, isobutylene, sec-butylene, tert-butylene, n-pentylene, sec-amylene, tert-amylene, hexylene, 2,2'-dimethylbutylene, heptylene, octylene, 2-ethylhexylene, 1,1',3,3'-tetramethylbutylene, nonylene, decylene, dodecylene, tetradecylene, hexadecylene, octadecylene, eicosylene, heneicosylene, docosylene, tetracosylene, pentacosylene, hexacosylene, heptacosylene, octacosylene or nonacosylene,

preference being given to C₁-C₁₈alkylene such as methylene, ethylene, propylene, isopropylene, n-butylene, isobutylene, sec-butylene, tert-butylene, n-pentylene, sec-amylene, tert-amylene, hexylene, 2,2'-dimethylbutylene, heptylene, octylene, 2-ethylhexylene, 1,1',3,3'-tetramethylbutylene, nonylene, decylene, dodecylene, tetradecylene, hexadecylene or octadecylene, and

particular preference to C₈-C₁₈alkylene such as octylene, 2-ethylhexylene, 1,1',3,3'-tetramethylbutylene, nonylene, decylene, dodecylene, tetradecylene, hexadecylene or octadecylene;

in addition, particular preference is given to C₁-C₈alkylene such as methylene, ethylene, propylene, isopropylene, n-butylene, isobutylene, sec-butylene, tert-butylene, n-pentylene, sec-amylene, tert-amylene, hexylene, 2,2'-dimethylbutylene, heptylene, octylene, 2-ethylhexylene or 1,1',3,3'-tetramethylbutylene.

C₅-C₁₂cycloalkyl is for example cyclopentyl, cyclohexyl, cycloheptyl or cyclooctyl, preferably C₅-C₆cycloalkyl such as cyclopentyl or cyclohexyl.

C₅-C₁₂cycloalkylene is for example cyclopentylene, cyclohexylene, cycloheptylene or cyclooctylene, preferably C₅-C₆cycloalkylene such as cyclopentylene or cyclohexylene.

Alkyl radicals or alkylene radicals of at least two carbon atoms, represented by R₁ or G₇, can be interrupted one or more times by for example -O-, -NH-, -C(O)O-, -O-C(O)-, -C(O)-NH-; preference is given to -C(O)O- or -O- and very particular preference to the -C(O)O- interrupted alkyl radical -CH₂-C(O)O-CH₂CH₃, or the singly -O-interrupted alkyl radical such as -CH₂-CH₂-O-CH₂-CH₃, or the doubly -O-interrupted alkyl radical such as -CH₂-CH₂-O-CH₂-O-CH₂-CH₃.

In addition, the alkyl or cycloalkyl radicals or the phenyl radical of R₁ can be substituted by, for example, the following radicals:

C₁-C₁₈alkyl, OR₃, S-R₃, C(O)R₃, COOR₃, -OCOR₃, SO₃R₃, SO₂R₃, PO₃R₃, Si(OR)₃, a salt radical such as S-M, O-M, COOM, SO₃M, PO₃M, P(R₃)₃⁺ X⁻, P((R₃)₂R₄)₃⁺ X⁻, NO₂, N(R₃)₃⁺ X⁻, N((R₃)₂R₄)₃⁺ X⁻ or a nitrogen-containing radical,

in which

R₃ and R₄ independently of one another are hydrogen, C₁-C₁₈alkyl, especially methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, sec-amyl, tert-amyl, hexyl or 2,2-dimethylbutyl, or are C₅-C₆cycloalkyl or unsubstituted or R₇-substituted phenyl,

M is a cation of an alkali metal, preferably sodium or potassium,

X⁻ is a halide, such as fluoride, chloride, bromide or iodide, and

R₇ is hydrogen, halogen such as F, Cl, Br, I or is C₁-C₈alkyl or unsubstituted or NR₃R₄-substituted C₅-C₆cycloalkyl.

Preferred OR₃ is OH, and preferred S-R₃ is SH.

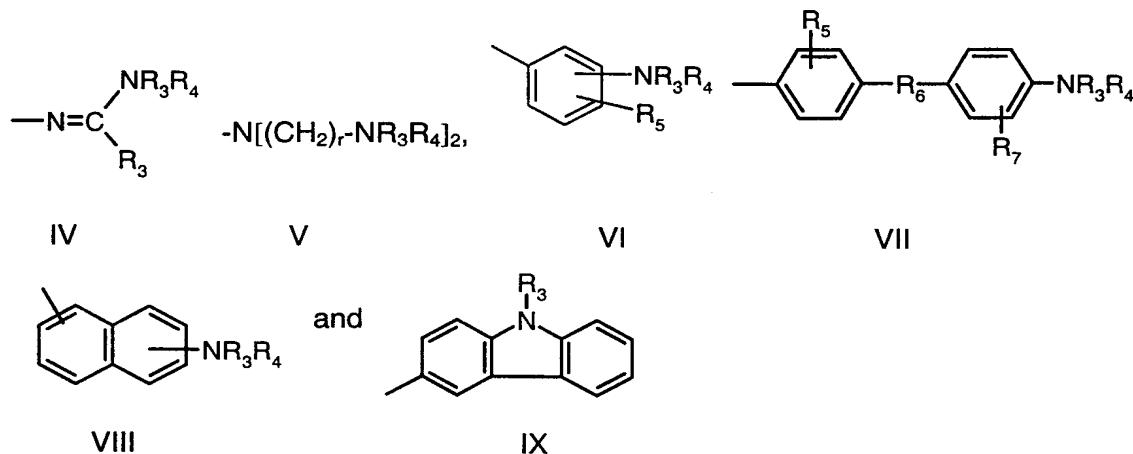
Preferred radicals COOR_3 are COOH , COOCH_3 , COOC_2H_5 , COOC_4H_9 , $\text{COOC}_5\text{H}_{11}$, and preferred $-\text{OCOR}_3$ is $-\text{O}-\text{CO}-\text{C}(\text{CH}_2)-\text{CH}_3$.

Preferred radicals SO_3R_3 are SO_3H , $\text{SO}_3(\text{C}_5\text{H}_4)\text{R}_7$, $\text{SO}_3(\text{C}_5\text{H}_5)$, SO_3CH_3 , $\text{SO}_3\text{C}_2\text{H}_5$, and preferred radicals SO_2R_3 are $\text{SO}_2(\text{C}_5\text{H}_4)\text{R}_7$, $\text{SO}_2(\text{C}_5\text{H}_4)$ or SO_2CH_3 .

Preferred radicals PO_3R_3 are PO_3H , $\text{PO}_3(\text{C}_5\text{H}_4)\text{R}_7$ or PO_3CH_3 .

Preferred nitrogen-containing radicals are selected from the group consisting of NR_3R_4 , especially NH_2 , NHR_3 or $\text{N}(\text{R}_3\text{R}_4)$, with particular preference being given to substituted alkyl radicals, such as $(\text{R}_3\text{R}_4)\text{N}-(\text{C}_1\text{-C}_{30}\text{alkyl})$ -, especially $(\text{CH}_3)_2\text{N-C}_2\text{H}_5$ -, further preferred nitrogen-containing radicals are selected from the group consisting of CONHNH_2 , CONHR_3 , NHCOR_3 , NCO and a heterocyclic radical and a compound selected from the group of the formulae IV to IX

a compound selected from the group of the formulae IV to IX



selected in particular from the group of the compounds of the formulae IV and V.

in which

R_5 independently of R_7 has the same definition as R_7 , and

R_6 is a direct bond, $-CH_2-$, $-CH(CH_3)-$, $-C(CH_3)_2-$, $-CH=N-$, $-N=N-$, $-O-$, $-S-$, $-SO-$, $-SO_2-$ or $-NR_3-$, and

r is zero or an integer from 1 to 17.

Furthermore, the alkylene, cycloalkylene or phenylene radical of G₇ can be substituted by, for example, the following radicals:

halogens such as fluorine, chlorine, bromine or iodine, preferably chlorine or bromine and, with particular preference, chlorine;

-E-C₁-C₁₈alkyl,

in which

E is -O-, -S-, -NH-, -C(O)O-, -OC(O)-, -NHC(O)-, -C(O)NH-;

CN, NO₂, CF₃ or C₁-C₁₈alkyl, which can be uninterrupted or interrupted one or more times by heteroatoms, such as -O- or -S-, or by -NH-, -C(O)O-, -O-C(O)- or -C(O)-NH-.

If E is -O-, then -O-C₁-C₁₈alkyl can be methoxy, ethoxy, n-propoxy, isopropoxy, hexadecyloxy or octadecyloxy, preferably methoxy or ethoxy and, with very particular preference, methoxy.

If E is -S-, then -S-C₁-C₁₈alkyl can be methylmercapto, ethylmercapto, n-propylmercapto, isopropylmercapto, hexadecylmercapto or octadecylmercapto, preferably methylmercapto or ethylmercapto and, with very particular preference, methylmercapto.

If E is -NH-, then -NH-C₁-C₁₈alkyl can be methylamine, ethylamine, n-propylamine, isopropylamine, hexadecylamine or octadecylamine, preferably methylamine or ethylamine and, with very particular preference, methylamine.

If E is -C(O)O- then -C(O)O-C₁-C₁₈alkyl can be methoxycarbonyl, ethoxycarbonyl, n-propoxycarbonyl, isopropoxycarbonyl, hexadecoxycarbonyl or octadecoxycarbonyl, preferably methoxycarbonyl or ethoxycarbonyl and, with very particular preference, methoxycarbonyl.

If E is -OC(O)- then -OC(O)-C₁-C₁₈alkyl can be a methyl, ethyl, n-propyl, isopropyl, hexadecyl or octadecyl ester radical, preferably a methyl or ethyl ester radical and, with very particular preference, a methyl ester radical.

If E is -C(O)NH- then -C(O)NH-C₁-C₁₈alkyl can be a methyl-, ethyl-, n-propyl-, isopropyl-, hexadecyl- or octadecylaminocarbonyl radical, preferably a methyl- or ethylaminocarbonyl radical and, with very particular preference, methyl- aminocarbonyl radical.

If E is -NHC(O)- then -NHC(O)-C₁-C₁₈alkyl can be a methyl-, ethyl-, n-propyl-, isopropyl-, hexadecyl- or octadecylcarbonylamino radical, preferably a methyl- or

ethylcarbonylamino radical and, with very particular preference, methylcarbonylamino radical.

Preferred substituted alkylene radicals for G₇ are symmetrically substituted radicals such as -(CH₂)_m-CH(C₁-C₃₀alkyl)-(CH₂)_m or -(CH₂)_m-C(C₁-C₃₀alkyl)₂-(CH₂)_m, in which m is an integer in the range from 1 to 14, with particular preference an integer in the range from 3 to 8.

Preferred substituted phenylene radical G₇ possesses one or two substituents such as halogen, C₁-C₁₈alkyl, -O-C₁-C₁₈alkyl, -S-C₁-C₁₈alkyl, -NH-C₁-C₁₈alkyl, CN, NO₂ or CF₃, where the substituents can be identical or different.

Heterocyclic radical is, for example, a five-membered nitrogen-containing heterocyclic radical such as imidazolyl, pyrazolyl, triazolyl, pyrrolyl, pyrrolidinyl, oxazolyl or thiazolyl, a six-membered nitrogen-containing heterocyclic radical such as piperazinyl, piperidinyl, pyridinyl or morpholinyl, or a bicyclic radical which possesses a fused-on five-membered nitrogen-containing heterocycle and a six-membered aromatic ring, such as benzoxazolyl, indolyl, benzothiazolyl, benzimidazolyl or benzotriazolyl.

Examples of suitable organic nitrogen bases for R₂ are pyridine, morpholine, N,N'-dimethylaminopyridine and quinoline.

Particular preference is given to thiols such as C₁-C₁₈alkyl-SH, especially H-S-(CH₂)_n-CH₃, in which n is an integer from 8 to 17, H-S-CH₂COOC₂H₅, H-S-CH₂CH₂COOC₂H₅, H-S-(para-methylphenyl), H-S-(para-hydroxyphenyl), and also H-S-(CH₂)_{n1}-NR₃R₄ in which n1 is an integer from 8 to 18, H-S-(CH₂)₂N(CH₃)₂, and also thiolates such as sodium salts or potassium salts of 'S-(C₁-C₁₈alkyl), 'S-(CH₂)₂-OH, 'S-CH₂COOC₂H₅, 'S-(para-methylphenyl), 'S-(para-hydroxyphenyl) or 'S-(CH₂)₂N(CH₃)₂.

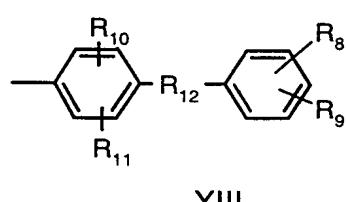
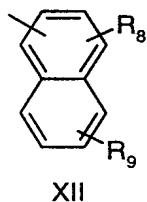
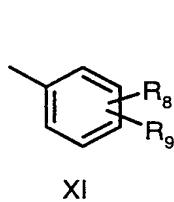
Particularly preferred dithiols are -S-(C₁-C₁₈alkylene)-S-, especially -S-(C₃-C₈alkylene)-S-, such as -S-(CH₂)₃-S-, -S-(CH₂)₄-S-, -S-(CH₂)₅-S-, -S-(CH₂)₆-S-, -S-(CH₂)₇-S- or -S-(CH₂)₈-S-, and very particularly preferred dithiols are -S-(CH₂)₃-S-, -S-(CH₂)₅-S- or -S-(CH₂)₆-S-.

The thiols, dithiols or thiolates, dithiolates of the formula IIIa or IIIb are obtainable commercially or by known methods for preparing thiols, dithiols or thiolates, dithiolates

(Houben-Weyl, Methoden der organischen Chemie, Volume E 11, pp. 32-63, Georg Thieme Verlag, Stuttgart, New York, 1985; and J.L. Wardell, "Preparation of Thiols", in S. PATAI (ed.), The chemistry of the thiol group, pp. 163-269, John Wiley & Sons, London, New York, 1974).

In the process of the invention a halo-DPP of the formula IIa is used in which G₂ is a halogenated phenyl group and G₃ is G₂ or G₁, and G₃ is preferably G₂ or a carbocyclic or heterocyclic radical and with particular preference is G₂; in other words, the halo-DPP of the formula IIa in that case is a symmetrically substituted halo-DPP.

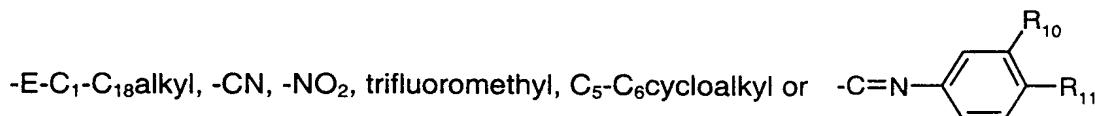
If G₃ or G₆ is G₁, then the radical involved can also be a heterocyclic radical which corresponds to the above definition of heterocyclic radicals and is additionally pyrimidine, thiophene or furan, or else the radical involved can be a carbocyclic group of the formula XI, XII or XIII



in which

R₈, R₉, R₁₀ and R₁₁

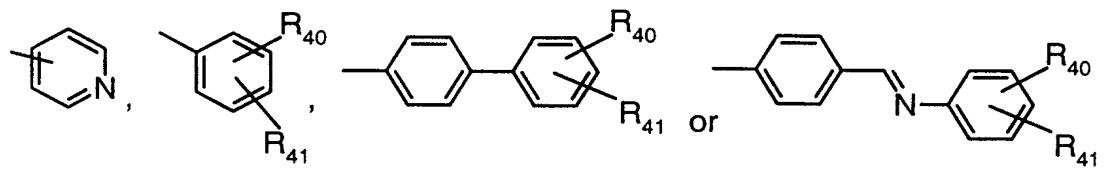
independently of one another are hydrogen, halogen such as fluorine, chlorine, bromine or iodine or C₁-C₁₈alkyl,



and in particular hydrogen, C₁-C₅alkyl such as methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, sec-amyl or tert-amyl, or halogen such as Cl or Br, and

R₁₂ is a single bond, -CH₂-, -CH(CH₃)-, -C(CH₃)₂-, -CH=N-, -N=N-, -O-, -S-, -SO-, -SO₂- or -NR₃-.

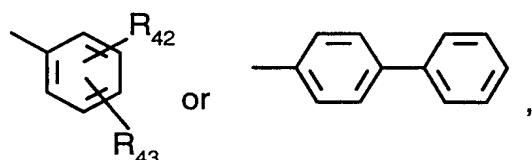
With particular preference, halo-DPP of the formula IIb together with G₆ is an organic radical such as



in which

R₄₀ and R₄₁ independently of one another are hydrogen, halogen such as fluorine, chlorine, bromine or iodine, or C₁-C₁₈alkyl, -E-C₁-C₁₈alkyl, -CN, -NO₂ or trifluoromethyl.

With very particular preference G₆ is an organic radical such as



in which

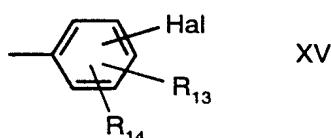
R₄₂ and R₄₃ independently of one another are hydrogen, chlorine, methyl, tert-butyl or -CN.

In one preferred embodiment the halogenated phenyl group G₂ employed is a compound of the formula XIV



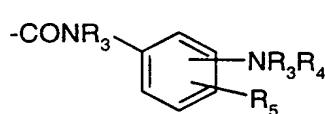
in which Hal is halogen such as fluorine, chlorine, bromine or iodine, preferably chlorine or bromine. With particular preference, halogen is in the para position.

If desired, the halogenated phenyl group G₂ can be a compound of the formula XV

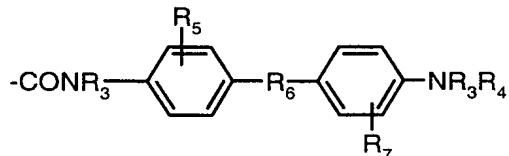


and can carry further substituents, R₁₃ or R₁₄, where R₁₃ and R₁₄ independently of one another are, for example,

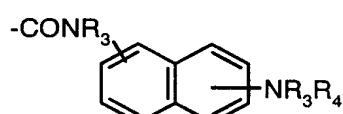
hydrogen, CN, CF₃, C₁-C₅alkyl, C₅-C₆cycloalkyl, -E-C₁-C₁₈alkyl, phenyl, S-R₁, amides such as -CONR₃R₄ or amides of the formulae XVI to XIX



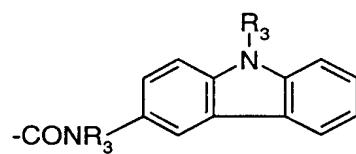
XVI



XVII



XVIII



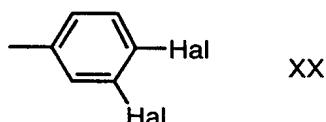
XIX

or amides of nitrogen-containing heterocycles such as 1-carbonyl-imidazole, -pyrazole, -triazole, -pyrrole, -pyrrolidine, -benzimidazole or -benzotriazole, or halogen such as fluorine, chlorine, bromine or iodine, preferably chlorine or bromine.

Preferably, R₁₃ and R₁₄ are in the meta positions.

In a further preference, R₁₄ is hydrogen and R₁₃ is one of the above substituents other than hydrogen, preferably in the meta position.

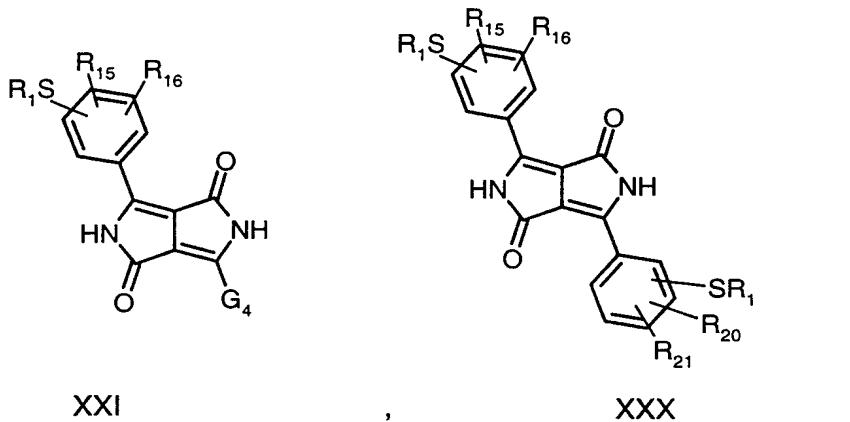
In another preferred embodiment the halogenated phenyl group G₂ is of the formula XX



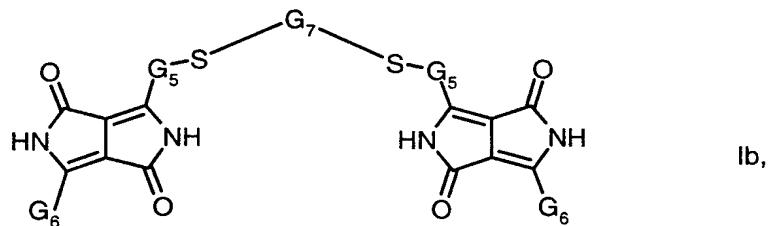
in which Hal is preferably fluorine, chlorine, bromine or iodine and, with particular preference, chlorine or bromine.

Halo-DPPs II with correspondingly substituted groups are known, for example, from patents US 5,484,943, US 5,616,725 or US 5,200,528 or are obtainable in accordance with US 4,579,949.

A further embodiment of the present invention relates to new DPPs of the formulae XXI and XXX



and to novel bis-DPPs of the formula Ib



in which R₁₅, R₁₆, R₂₀ and R₂₁ independently of one another are hydrogen or R₁₃ or R₁₄, and G₄ is a carbocyclic or heterocyclic radical, with the proviso that (a) R₁ in formula XXI is not phenyl if R₁₅ and R₁₆ are hydrogen and G₄ is phenyl, and (b) R₁ in formula XXX is not phenylene(C₁-C₄alkyl) or C₁-C₁₂alkyl if R₁₅, R₁₆, R₂₀ and R₂₁ are hydrogen, and G₅ is a phenylene, G₆ is a carbocyclic or heterocyclic radical, and G₇ is alkylene, cycloalkylene or phenylene.

Preferred DPPs of the formula XXI or XXX are those in which R₁ is mono- or polysubstituted or unsubstituted C₁-C₃₀alkyl or a phenyl radical.

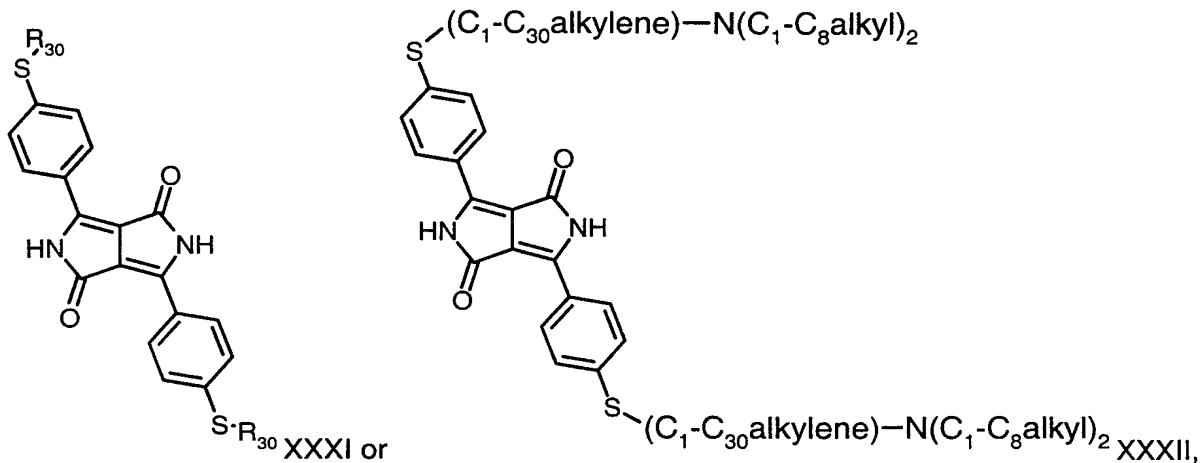
With particular preference, R₁₅, R₁₆, R₂₀ and R₂₁ are hydrogen and R₁ is -C₁-C₁₈alkyl, such as C₄alkyl, C₆alkyl, C₉alkyl, C₁₂alkyl or C₁₈alkyl, and also -(para-

phenylene)-OH, -CH₂CH₂OH, -CH₂C(O)O-CH₂CH₃, -(CH₂)₂C(O)O-CH₂CH₃ - (C₁-C₃₀alkylene)-N(R₃,R₄) such as -(C₂H₅)-N(CH₃)₂.

Particular preference is given to compounds of the formula Ib in which G₅ is 1,4-phenylene and G₇ is n-propylene, n-butylene, n-pentylene, n-hexylene, n-heptylene or n-octylene, or substituted or unsubstituted phenylene and G₆ is unsubstituted or substituted phenyl.

Very particular preference is given to compounds of the formula Ib in which G₅ is 1,4-phenylene and G₇ is n-propylene, n-butylene, n-pentylene, n-hexylene, n-heptylene or n-octylene and G₆ is unsubstituted phenyl.

Very particular preference is given to compounds of the formula XXXI or XXXII



in which

R₃₀ is C₁-C₃₀alkyl, with particular preference C₁-C₁₈alkyl and, with very particular preference, C₅-C₁₈alkyl.

A further embodiment of the present invention relates to compositions comprising a DPP of the formula Ia and a halo-DPP of the formula IIa, obtainable by the process of the invention using a substoichiometric amount of thiol or thiolate of the formula IIIa. Preferably, the thiol or thiolate of the formula IIIa is employed in a molar ratio that is within the range from 0.1 to 49%, based on the total amount of thiol or thiolate of the formula IIIa and halo-DPP of the formula IIa.

A further embodiment of the process of the invention relates to compositions comprising at least two differently substituted DPPs of the formula Ia. These compositions are obtainable either by reacting at least two differently substituted halo-DPPs of the formula IIa with a thiol or thiolate of the formula IIIa or, conversely, by reacting at least two differently substituted thiols or thiolates of the formula IIIa with a halo-DPP of the formula IIa.

The molar ratio of thiol or thiolate of the formula IIIa to differently substituted halo-DPPs of the formula IIa, or of differently substituted thiols or thiolates of the formula IIIa to halo-DPP of the formula IIa, is generally chosen to be within the range from 20:0.1 to 1:1, preferably in the range from 10:1 to 5:1 and, with very particular preference, within the range from 5:1 to 5:2.

The molar ratio of the differently substituted halo-DPPs of the formula IIa to one another is generally chosen to be within the range from 0.1 to 99.9 mol-%, based on the total amount of differently substituted halo-DPPs of the formula IIa, and is preferably in the range from 20 to 80 mol-% and, with particular preference, in the range from 40 to 60 mol-%.

The molar ratio of differently substituted thiols or thiolates of the formula IIIa to one another is generally chosen to be within the range from 0.1 to 99.9 mol-%, based on the total amount of differently substituted thiols or thiolates of the formula IIIa, is preferably within the range from 20 to 80 mol-% and, with particular preference, in the range from 40 to 60 mol-%.

The invention relates, furthermore, to compositions comprising a DPP of the formula XXI and/or XXX and/or DPP Ia and/or Ib and diketo-diaryl-pyrrolopyrrole (DPP) or a DPP latent pigment, wherein DPPs of formula XXI and Ia, or XXX and Ib are different. DPP latent pigments are described, for example, in US 5,616,725. In a preferred embodiment, the molar ratio of DPP of the formula XXI and/or XXX to DPP, DPP of the formula Ia or Ib, or DPP latent pigment is chosen to be within the range from 0.1 to 99.9 mol-%, based on the total amount of DPP of the formula XXI or XXX, DPP or DPP latent pigment, more preferably from 20 to 80 mol-% and, with particular preference, from 40 to 60 mol-%.

These compositions of the invention can be prepared by customary methods, for example, by mixing the individual components with one another in accordance with the customary methods, in analogy, for example, to the method described in US 5,200,528.

The DPPs can be prepared by customary methods as described in US 5,200,528. Similarly, the DPP latent pigments can be prepared in analogy to the method described in US 5,561,232.

Furthermore, the invention relates to the use of DPP of the formula Ia and/or Ib as rheology enhancers or as crystal growth inhibitors.

A further embodiment of the present invention relates to the use of DPPs of the formula XXI or XXX as rheology enhancers or as crystal growth inhibitors.

In addition, the invention relates to a rheology enhancer or crystal growth inhibitor comprising DPP of the formula Ia and/or Ib.

In common practice the rheology enhancers or crystal growth inhibitors are used in compositions comprising DPP of the formula Ia and/or Ib and DPP or DPP latent pigment.

A further embodiment of the present invention relates to compositions comprising DPP of the formula Ia and/or Ib and DPP or DPP latent pigment.

The present invention relates further to a method of enhancing rheology or of inhibiting crystal growth which comprises incorporating an effective amount of DPP of the formula Ia and/or Ib in DPP or a DPP latent pigment.

The molar ratio of DPP of the formula Ia and/or Ib is usually in the range from 0.1 to 20 mol-% based on of DPP of the formula Ia and/or Ib and DPP or DPP latent pigment.

Furthermore, the present invention relates to the use of DPP of the formula XXI or XXX or bis-DPP Ib, or of a composition comprising a DPP of the formula XXI and/or XXX and/or DPP Ia and/or Ib and diketo-diaryl-pyrrolopyrrole (DPP) or a DPP latent pigment, wherein DPPs of

formula XXI and Ia, or XXX and Ib are different, for colouring/pigmenting high molecular mass organic material.

The invention additionally relates to a method of colouring/pigmenting high molecular mass organic material which comprises incorporating a colouristically effective amount of DPP of the formula XXI or XXX or of bis-DPP Ib, or of a composition comprising a DPP of the formula XXI and/or XXX and/or DPP Ia and/or Ib and diketo-diaryl-pyrrolopyrrole (DPP) or a DPP latent pigment, wherein DPPs of formula XXI and Ia, or XXX and Ib are different, therein, by conventional methods, as described, for example, in US 5,200,528.

In addition, the invention relates to compositions comprising high molecular mass organic material and DPP of the formula XXI or XXX or bis-DPP of the formula Ib.

In general the weight ratio of DPP of the formula XXI or XXX or bis-DPP of the formula Ib or the compositions of the invention is from 0.01 to 30% by weight, preferably from 0.1 to 10% by weight, based on the high molecular mass organic material.

Another preferred embodiment of the present invention relates to compositions consisting of high molecular mass organic material and DPP of the formula XXI or XXX or bis-DPP of the formula Ib and also

compositions consisting of DPP of the formula XXI or XXX or bis-DPP of the formula Ib and/or high molecular mass organic material and/or DPP of the formula Ia and also compositions consisting of DPP of the formula XXI or XXX and/or high molecular mass organic material and/or DPPs and also

compositions consisting of DPP of the formula XXI or XXX and/or high molecular mass organic material and/or DPP latent pigments and also

compositions consisting of DPP of the formula XXI or XXX and/or high molecular mass organic material and/or halo-DPP of the formula IIa and also

compositions consisting of DPP of the formula Ib and/or high molecular mass organic material and/or halo-DPP of the formula IIb.

High molecular mass organic materials can be of natural or synthetic origin. They may, for example, comprise natural resins or drying oils, rubber or casein, or modified natural substances, such as cellulose ethers or esters, cellulose acetate, cellulose propionate, cellulose acetobutyrate or nitrocellulose, and especially entirely synthetic organic polymers (thermosets and thermoplastics) as obtained by addition polymerization, polycondensation,

or polyaddition. From the class of the addition-polymerization resins mention may be made primarily of polyolefins, such as polyethylene, polypropylene or polyisobutylene, and also substituted polyolefins, such as addition polymers of vinyl chloride, vinyl acetate, styrene, acrylonitrile, acrylates and/or methacrylates or butadiene, and also addition copolymers of the abovementioned monomers, especially acrylonitrile-butadiene-styrene (ABS) or ethylene-vinyl acetate (EVA).

From the series of the polyaddition resins and polycondensation resins mention may be made of the condensation products of formaldehyde with phenols, known as phenolic resins, and of the condensation products of formaldehyde with urea, thiourea and melamine, known as amino resins, the polyesters used as film-forming resins, both saturated, such as alkyd resins, and unsaturated, such as maleate resins, and also the linear polyesters and polyamides, and silicones.

The abovementioned high molecular mass organic materials can be present individually or in mixtures, as plastic masses or melts which can if desired be spun to fibre.

They can also be present in the form of their monomers or in the polymerized state in dissolved form as film formers or binders for coating materials or printing inks, such as linseed oil varnish, nitrocellulose, alkyd resins, melamine resins and urea-formaldehyde resins, or acrylic resins.

The colouring/pigmentation of the high molecular mass organic substances with the DPPs of the formula XXI or XXX or bis-DPP of the formula Ib or compositions of the invention comprising them takes place in general with the resultant crude product of the process of the invention, or following appropriate conditioning and aftertreatment, for example, in such a way that DPP of the formula XXI or XXX or bis-DPP of the formula Ib or compositions of the invention comprising them, as they are or in the form of master batches, are admixed to these substrates using roll mills or mixing or milling apparatus. The coloured/pigmented material is generally brought into the desired final form by techniques known per se, such as callendering, compression moulding, extrusion, spreading, pouring or injection moulding. It is often desirable, in order to produce nonrigid mouldings or to reduce their brittleness, to add plasticizers to the high molecular mass compounds prior to their forming. Examples of such plasticizers are esters of phosphoric, phthalic or sebatic acid. The plasticizers can be incorporated into the polymers before or after the incorporation of the colorant. It is also

possible, in order to obtain different shades, to add fillers and/or other colouring constituents, such as white, coloured or black pigments in the desired amount to the high molecular mass organic substances in addition to DPPs of the formula XXI or XXX or bis-DPPs of the formula Ib.

For pigmenting coating materials and printing inks, the high molecular mass organic materials and DPPs of the formula XXI or XXX or bis-DPP of the formula Ib or compositions of the invention comprising them alone or together with additives such as fillers, other pigments, siccatives or plasticizers are customarily dissolved or finely dispersed in a common organic solvent or solvent mixture. In this context it is possible to follow a procedure whereby the individual components are dispersed or dissolved individually or else two or more are dissolved or dispersed together and only then are all the components combined.

The resultant brightly coloured/pigmented high molecular mass materials, examples being plastics, fibres, coatings and prints, are notable for very high colour strength, high saturation, good dispersibility, high fastness to overcoating, heat, light and weather, and high lustre.

The process of the invention allows the preparation of a broad range of thio-substituted DPPs of the formula Ia, and even of long-chain alkylthio-DPPs and water-soluble DPPs, and also of dithio-bridged bis-DPPs of the formula Ib. The DPPs of the formula Ia, the bis-DPPs of the formula Ib and the compositions of the invention comprising a DPP of formula XXI or XXX are colorants of high lustre and transparency. The DPPs of the formula Ia and also the compositions of the invention comprising a DPP of formula XXI or XXX are particularly suitable for inhibiting crystal growth and enhancing rheology. The novel compounds or compositions and the compounds prepared by the process of this invention have good warp fastness properties in high molecular weight material, in particular in material that is processed by the injection moulding process using the novel compounds or compositions. Preferred high molecular weight materials are, for example, polyolefins. The high yields obtained with the process of the invention, and its simplicity, which permits operation without elevated pressure and without catalysts, moreover, are a guarantee of good economics.

Examples:

Example 1: Reaction of 1-octadecanethiol with diketobis(4-chlorophenyl)pyrrolopyrrole (DPP of the formula XXII, = halo-DPP of the formula IIa with $G_2 = G_3 =$ para-Cl-phenyl)

17.19 g (60 mmol) of 1-octadecanethiol dissolved in 60 ml of dimethylacetamide, DMA, are added dropwise under nitrogen to a red suspension of 10.72 g (30 mmol) of DPP XXII and 9.95 g (72 mmol) of potassium carbonate in 260 ml of DMA. The resultant mixture is then heated at 393 K for 24 hours, during which it turns violet.

Workup and isolation:

The reaction mixture is cooled to room temperature and then poured into 60 ml of ice water. The aqueous reaction mixture is filtered. The filter residue is washed with methanol and then with water and subsequently dried in vacuo at 353 K. This gives 24.37 g (94.7% of theory by weight) of a red pigment.

Examples 2-10: see Tables 1, 2, 3 and 4 below

Examples 11-21:

The reactions take place in analogy to that of Example 1 but, in contradistinction to Example 1, using instead of the DPP of the formula XXII

in Example 11 diketo-4,4'-dibromo(diphenyl)pyrrolopyrrole (DPP of the formula IIa with $G_2 = G_3 =$ para-Br-phenyl);

in Examples 12 and 13 diketo-4,4',3,3'-tetrachloro(diphenyl)pyrrolopyrrole (DPP of the formula IIa with $G_2 = G_3 =$ para,meta-dichlorophenyl);

in Example 14 diketo-4-chloro(diphenyl)pyrrolopyrrole, (DPP of the formula IIa with $G_2 \neq G_1$; $G_2 =$ para-chlorophenyl and $G_1 =$ phenyl);

in Example 15 diketo-4-chloro-4-methyl(diphenyl)pyrrolopyrrole (DPP of the formula IIa with $G_2 \neq G_1$; $G_2 =$ para-chlorophenyl and $G_1 =$ para-methylphenyl);

in Example 16 diketo-4-chloro-4-tert-butyl(diphenyl)pyrrolopyrrole (DPP of the formula IIa with $G_2 \neq G_1$; $G_2 =$ para-chlorophenyl and $G_1 =$ para-tert-butylphenyl);

in Example 17 diketo-4-chloro-4-phenyl(diphenyl)pyrrolopyrrole (DPP of the formula IIa with $G_2 \neq G_1$; $G_2 =$ para-chlorophenyl and $G_1 =$ para-phenylphenyl);

in Example 18 diketo-3-bromo(diphenyl)pyrrolopyrrole (DPP of the formula IIa with $G_2 \neq G_1$; $G_2 =$ meta-bromophenyl and $G_1 =$ phenyl);

in Examples 19-21 (preparation of bis-DPP) diketo-4-chloro-4-phenyl(diphenyl)pyrrolopyrrole (DPP of the formula IIb with G_2 = para-chlorophenyl and G_6 = phenyl) is employed and in Examples 22-28 the reaction takes place in analogy to that of Example 1 but, in contradistinction to Example 1, using instead of the DPP of the formula XXII

in Example 22 (composition comprising a halo-DPP XXII and a DPP IIa with $G_2 = G_3 =$ para-Cl-phenyl) thiol in a substoichiometric amount with respect to halo-DPP XXII, and

in Example 23 using in this case 1,3-dimethyl-3,4,5,6-tetrahydro-3(1H)pyrimidinone instead of the solvent DMA, and

in Examples 24-28 varying the bases.

Table 1: Examples 1-28, whose reaction takes place in analogy to that of Example 1, the altered starting materials, experimental parameters and yields being indicated in the table.

Example	Amount of DPP (g)	Thiol	Amount of thiol dissolved in solvent (ml)	Amount of solvent (ml)	Base	Amount of base (g)	Reaction time /temp. (h)/(K)
1	10.72	1-octa-decanethiol	17.19 g in 60 ml DMA	260 ml DMA	K ₂ CO ₃	9.95	24/393
2	10.72	2-mercaptop-ethanol	4.21 ml in 40 ml DMA	260 ml DMA	K ₂ CO ₃	9.95	2/393
3	10.72	1-nonane-thiol	9.62 ml in 40 ml DMA	260 ml DMA	K ₂ CO ₃	9.95	4.5/403
4	10.72	ethyl thio-glycolate	7.24 g in 40 ml **DMSO	260 ml **DMSO	K ₂ CO ₃	9.95	19/371
5	10.72	p-methyl-thiophenol	7.45 g in 40 ml DMA	260 ml DMA	K ₂ CO ₃	9.95	18.5/383
6	10.72	4-mercaptop-phenol	9.25 g in 40 ml DMA	260 ml DMA	K ₂ CO ₃	9.95	17/393-403
7	10.02	1-propane-thiol	6.39 g in 30 ml DMA	230 ml DMA	K ₂ CO ₃	9.28	19.5/403
8	10.72	1-dodecane-thiol	15.18 g in 50 ml DMA	350 ml DMA	K ₂ CO ₃	10.36	16/393
9	5.36	2-dimethyl-amino-ethanethiol	6.37 g in 40 ml **DMSO	130 ml **DMSO	K ₂ CO ₃	4.98	22.5/383
10	5.36	1-hexane-thiol	3.55 g in 40 ml DMA	170 ml DMA	K ₂ CO ₃	4.98	18.3/393
11	5.35	1-octa-decanethiol	10.32 g in 20 ml DMA	130 ml DMA	K ₂ CO ₃	4.98	6.25/413
12	2.34	1-nonane-thiol	5.29 g in 10 ml DMA	70 ml DMA	K ₂ CO ₃	1.82	18.5/393

Example	Amount of DPP (g)	Thiol	Amount of thiol dissolved in solvent (ml)	Amount of solvent (ml)	Base	Amount of base (g)	Reaction time /temp. (h)/(K)
13	2.34	1-nonane-thiol	5.29 in 10 ml DMSO**	80 ml DMSO**	K ₂ CO ₃	1.82	18.5/393
14	9.04	2-dimethyl-amino-ethanethiol	8.35 g in 30 ml DMSO**	250 ml DMSO**	K ₂ CO ₃	1.82	20/373
15	10.1	2-dimethyl-amino-ethanethiol	8.35 g in 30 ml DMSO**	250 ml DMSO**	K ₂ CO ₃	1.82	20/373
16	5.68	2-dimethyl-amino-ethanethiol	8.35 g in 30 ml DMSO**	250 ml DMSO**	K ₂ CO ₃	1.82	20/373
17	9.97	2-dimethyl-amino-ethanethiol	8.35 g in 30 ml DMSO**	250 ml DMSO**	K ₂ CO ₃	1.82	20/373
18	4.04	1-octadecanethiol	6.3 g in 10 ml DMA	130 ml DMA	K ₂ CO ₃	3.65	6/403
19	4.84	1,3-propane-dithiol	1.62 g	100 ml DMA	K ₂ CO ₃	2.9	6/380
20	4.84	1,5-pentane-dithiol	2.04 g	100 ml DMA	K ₂ CO ₃	2.9	6/380
21	4.84	1,5-hexane-dithiol	1.41 g	100 ml DMA	K ₂ CO ₃	2.9	6/380
22	5.36	2-dimethyl-amino-ethanethiol	1.06 g in 20 ml DMSO	130 ml DMSO	K ₂ CO ₃	2.07	0.5/353
23	10.72	1-octadecanethiol	17.19 g in 60 ml ^	260 ml ^	K ₂ CO ₃	9.95	24/393

Example	Amount of DPP (g)	Thiol	Amount of thiol dissolved in solvent (ml)	Amount of solvent (ml)	Base	Amount of base (g)	Reaction time /temp. (h)/(K)
24	10.72	1-octa-decanethiol	17.19 g in 60 ml	260 ml	Na ₂ CO ₃	9.95	24/393
25	10.72	1-octa-decanethiol	17.19 g in 60 ml	260 ml	KHCO ₃	9.95	24/393
26	10.72	1-octa-decanethiol	17.19 g in 60 ml	260 ml	Na	9.95	24/393
27	10.72	1-octa-decanethiol	17.19 g in 60 ml	260 ml	KOH	9.95	24/393
28	10.72	1-octa-decanethiol	17.19 g in 60 ml	260 ml	NaOH	9.95	24/393

** DMSO is dimethyl sulfoxide

^ 1,3-Dimethyl-3,4,5,6-tetrahydro-3(1H)pyrimidinone

Table 2: Examples 1-28, whose workup and isolation takes place in analogy to that of

Example 1:

Example	Amount of ice water (ml)	Methanol (ml)	Water	Drying temperature (K)	Yield (g/% of theory by weight)
1	600	+	+	353	24.37g/ 94.7%
2	600	300*	+	353	12.21g/ 92.4%
3	600	-	(1.5 l)	353	16.83 g/ 92.7%
4	600***	+	+	343	12.65 g/ 80.4%

Example	Amount of ice water (ml)	Methanol (ml)	Water	Drying temperature (K)	Yield (g/% of theory by weight)
5	600	+	(1 l)	343	14.96 g/ 93.4%
6	600	(150 ml)	-	343	15.17 g/ 94.2%
7	500	(1.5 l)	(1.5 l)	343	9.98 g/ 81.4%
8	700	(1 l)	(0.8 l)	353	19 g/ 92.1%
9	300	(1 l)	(0.5 l)	343	7.12 g/ 96.0%
10	300	(1 l)	(0.5 l)	343	7.11 g/ 91.0%
11	300	(1.5 l)****	(1 l)****	343	8.5 g/ 82.6%
12	200	-	(0.5l) *****	343	1.82 g/ 49.1%
13	200	-	(0.5l) *****	343	2.41 g/ 65.0%
14	500	+ (1.5 l)	+ (1 l)	343	10.6 g/ 96.7%
15	500	+ (1.5 l)	+ (1 l)	343	11.88 g/ 97.65%
16	500	(1.5 l)	(1 l)	343	6.6 g/ 98%
17	500	(1.5 l)	(1 l)	343	10.76 g/ 92%
18	300	(1.5 l)	(0.75 l)	343	5.74 g/ 91.1%
19	200	(0.5 l)	(0.2 l) *****	343	4.53 g/ 88.7%

Example	Amount of ice water (ml)	Methanol (ml)	Water (0.2 l) *****	Drying temperature (K)	Yield (g/% of theory by weight)
20	200	(0.5 l)	(0.2 l) *****	343	5.22 g/ 98.2%
21	200	(0.5 l)	(0.2 l) *****	343	5.27 g/ 97.2%
22	300	(0.5 l)	*****	343	4.97 g
23	600	+	+	353	94%
24	600	+	+	353	99%
25	600	+	+	353	95%
26	600	+	+	353	96%
27	600	+	+	353	98%
28	600	+	+	353	99%

"+" means: component is used in the reaction

"-" means: component is not used in the reaction

*Example 2: The filter residue is taken up in 300 ml of methanol and stirred at room temperature, T 295 K, for 12 h. The methanolic reaction mixture is filtered. The filter residue is washed with water.

***Example 4: The reaction mixture is poured into 600 ml of ice water and neutralized with concentrated hydrochloric acid until the pH reaches 7. The aqueous reaction mixture is filtered. The filter residue is washed with methanol and water.

****Example 11: After the filter residue has been washed with methanol and then with water, it is admixed with ethyl acetate, heated to boiling temperature and stirred at this temperature for 2 hours. The reaction mixture is subsequently filtered and the filter residue is dried in vacuo at 343 K.

***** Examples 12 and 13: After the filter residue has been washed with water, it is admixed with ethyl acetate, heated to boiling temperature and stirred at this temperature for 6 hours. The reaction mixture is subsequently filtered and the filter residue is dried in vacuo at 343 K.

***** Examples 19-21: As under ***** but using DMA in this case instead of ethyl acetate.

***** Example 22: After the filter residue has been washed with water, it is admixed with 300 ml of methanol/water (1:1) and stirred at room temperature. The reaction mixture is

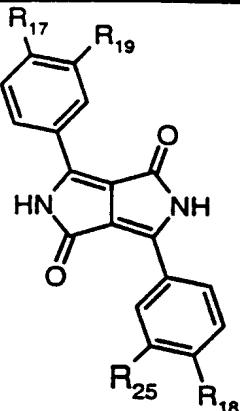
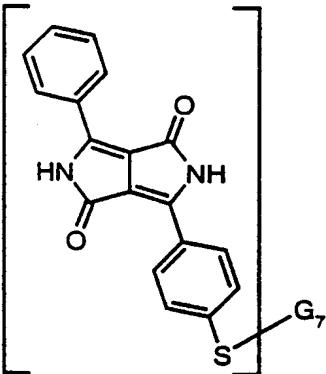
subsequently filtered and the filter residue is washed with 300 ml of methanol and then with 300 ml of water and subsequently dried in vacuo at 343 K.

Table 3: Elemental analyses of Examples 1-21

	Analysis:	C	H	N	Cl	S
<u>Example 1:</u>	calculated: found:	75.65% 75.61%	9.87% 9.67%	3.27% 3.38%	- -	7.48% 7.46%
<u>Example 2:</u>	calculated: found:	59.98% 59.67%	4.58% 4.66%	6.36% 6.25%	- -	14.56% 14.66%
<u>Example 3:</u>	calculated: found:	71.48% 71.40%	8.00% 8.10%	4.63% 4.38%	- -	10.60% 10.46%
<u>Example 4:</u>	calculated: found:	59.53% 59.74%	4.61% 4.16%	5.34% 6.05%	- -	12.22% 12.22%
<u>Example 5:</u>	calculated: found:	72.16% 72.25%	4.54% 4.54%	5.26% 5.25%	- -	12.04% 11.96%
<u>Example 6:</u>	calculated: found:	67.15% 65.73%	3.76% 4.19%	5.22% 5.52%	- -	11.95% 11.24%
<u>Example 7:</u>	calculated: found:	66.03% 66.17%	5.54% 5.43%	6.42% 6.66%	- -	14.69% 14.75%
<u>Example 8:</u>	calculated: found:	73.21% 73.08%	8.87% 8.49%	4.07% 4.11%	- -	9.31% 9.28%
<u>Example 9:</u>	calculated: found:	63.13% 63.17%	6.11% 6.13%	11.33% 10.73%	- -	12.96% 13.03%
<u>Example 10:</u>	calculated: found:	69.19% 69.96%	6.97% 6.88%	5.38% 5.64%	- -	12.31% 11.49%
<u>Example 11:</u>	calculated: found:	75.65% 75.63%	9.87% 9.84%	3.27% 3.36%	- -	7.48% 7.30%
<u>Example 12:</u>	calculated: found:	64.17% 63.66%	6.88% 6.83%	4.16% 4.35%	10.52% 10.68%	9.52% 9.07%
<u>Example 13:</u>	calculated: found:	69.19% 69.96%	6.97% 6.88%	5.38% 5.64%		12.31% 11.49%
<u>Example 14:</u>	calculated: found:	69.19% 69.96%	6.97% 6.88%	5.38% 5.64%		12.31% 11.49%

	Analysis:	C	H	N	Cl	S
<u>Example 15:</u>	calculated: found:	69.19% 69.96%	6.97% 6.88%	5.38% 5.64%		12.31% 11.49%
<u>Example 16:</u>	calculated: found:	69.19% 69.96%	6.97% 6.88%	5.38% 5.64%		12.31% 11.49%
<u>Example 17:</u>	calculated: found:	69.19% 69.96%	6.97% 6.88%	5.38% 5.64%		12.31% 11.49%
<u>Example 18:</u>	calculated: found:	69.19% 69.96%	6.97% 6.88%	5.38% 5.64%		12.31% 11.49%
<u>Example 19:</u>	calculated: found:	68.81% 68.82%	4.15% 3.99%	8.23% 8.37%		9.42% 9.56%
<u>Example 20:</u>	calculated: found:	69.47% 69.32%	4.55% 4.71%	7.9% 7.86%		9.05% 9.52%
<u>Example 21:</u>	calculated: found:	69.79% 69.32%	4.74% 4.63%	7.75% 7.67%		8.87% 9.43%

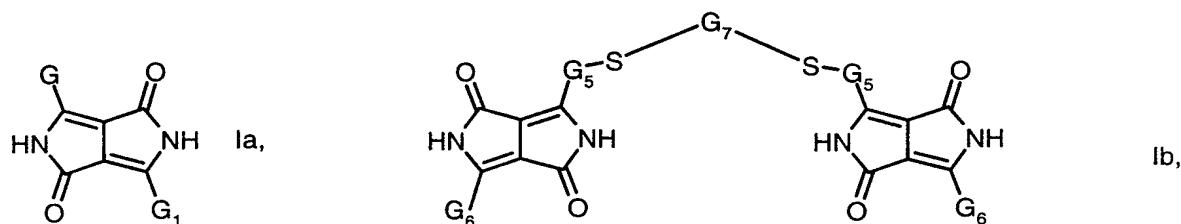
Table 4: List of compounds of Examples 1 to 28

	Examples	 2	Examples
$R_{17}, R_{18} = -S-(CH_2)_{17}CH_3$ $R_{19}, R_{25} = H$	1, 23-28 and 22 (Example 22 composition with halo-DPP)	$G_7 = \text{propylene}$	19
$R_{17}, R_{18} = -S-(CH_2)_2OH$ $R_{19}, R_{25} = H$	2	$G_7 = \text{pentylene}$	20
$R_{17}, R_{18} = -S-(CH_2)_8CH_3$ $R_{19}, R_{25} = H$	3	$G_7 = \text{hexylene}$	21
$R_{17}, R_{18} = -S-CH_2-COO-$ CH_2CH_3 $R_{19}, R_{25} = H$	4		
$R_{17}, R_{18} = -S\text{-phenyl-}(para-$ methyl) $R_{19}, R_{25} = H$	5		
$R_{17}, R_{18} = -S\text{-phenyl-}(para-$ hydroxy) $R_{19}, R_{25} = H$	6		
$R_{17}, R_{18} = -S-(CH_2)_2CH_3$ $R_{19}, R_{25} = H$	7		
$R_{17}, R_{18} = -S-(CH_2)_{11}CH_3$			

	Examples
$R_{17}, R_{18} = -S-(CH_2)_2N(CH_3)_2$ $R_{19}, R_{25} = H$	9
$R_{17}, R_{18} = -S-(CH_2)_5CH_3$ $R_{19}, R_{25} = H$	10
$R_{17}, R_{18} = -S-(CH_2)_{17}CH_3$ $R_{19}, R_{25} = H$	11
$R_{17}, R_{18} = -S-(CH_2)_8CH_3$ $R_{19}, R_{25} = Cl$	12, 13
$R_{17} = -S-(CH_2)_2N(CH_3)_2$ $R_{19}, R_{25}, R_{18} = H$	14
$R_{17} = -S-(CH_2)_2N(CH_3)_2$ $R_{19}, R_{25} = H$ $R_{18} = -CH_3$	15
$R_{17} = -S-(CH_2)_2N(CH_3)_2$ $R_{19}, R_{25} = H$ $R_{18} = -C(CH_3)_3$	16
$R_{17} = -S-(CH_2)_2N(CH_3)_2$ $R_{19}, R_{25} = H$ $R_{18} = -phenyl$	17
$R_{19} = -S-(CH_2)_{17}CH_3$ $R_{17}, R_{25}, R_{18} = H$	18

WHAT IS CLAIMED IS:

1. A process for preparing an alkylthio- and/or arylthio-substituted diketo-diaryl-pyrrolopyrrole (DPP) of the formula Ia or a dithio-bridged bis-diketo-diaryl-pyrrolopyrrole (bis-DPP) of the formula Ib



in which in formula Ia

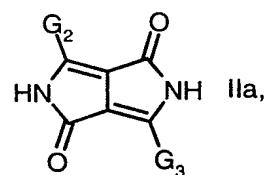
G is phenyl substituted by at least one arylthio or alkylthio group, and

G₁ is G or a carbocyclic or heterocyclic radical, by reacting a haloaryl with a thiol or thiolate, and

in formula Ib

G₅ is a phenylene, G₆ is G₁ but not G, and G₇ is alkylene, cycloalkylene or phenylene, by reacting two haloaryls with a dithiol or dithiolate,

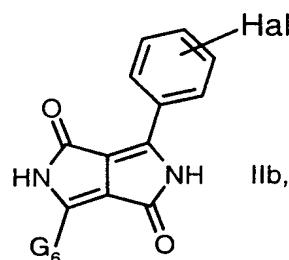
which comprises reacting a thiol or thiolate with a halo-diketo-diaryl-pyrrolopyrrole ("halo-DPP") of the formula IIa



in which

G₂ is a halogenated phenyl group and G₃ is G₂ or G₁, or

reacting a dithiol or dithiolate with two halo-diketo-diaryl-pyrrolopyrroles ("halo-DPPs") of the formula IIb



in which Hal is halogen such as fluorine, chlorine, bromine or iodine.

2. A process according to claim 1, wherein the thiol or thiolate employed is a compound of the formula IIIa or a dithiol or dithiolate of the formula IIIb



in which

R_1 can be C_1-C_{30} alkyl which can be uninterrupted or interrupted one or more times by heteroatoms, such as -O- or -S-, or by -NH-, -C(O)O-, -O-C(O)- or -C(O)-NH-, and can be substituted or unsubstituted, or can be C_5-C_{12} cycloalkyl or phenyl, each of which can be substituted or unsubstituted, and

R_2 is hydrogen, a cation ("M") of an alkali metal, or an organic nitrogen base, and

G_7 can be C_1-C_{30} alkylene which can be uninterrupted or interrupted one or more times by heteroatoms, such as -O- or -S-, or by -NH-, -C(O)O-, -O-C(O)- or -C(O)-NH-, and can be substituted or unsubstituted, or can be C_5-C_{12} cycloalkylene or phenylene, each of which can be substituted or unsubstituted.

3. A process according to claim 2, wherein the substituents of the alkyl radical, of the cycloalkyl radical or of the phenyl radical are

C_1-C_{18} alkyl, OR_3 , $S-R_3$, $C(O)R_3$, $COOR_3$, $-OCOR_3$, SO_3R_3 , SO_2R_3 , PO_3R_3 , $Si(OR)_3$, a salt radical such as $S-M$, $O-M$, $COOM$, SO_3M , PO_3M , $P(R_3)_3^+ X^-$, $P((R_3)_2 R_4)_3^+ X^-$, NO_2 , $N(R_3)_3^+ X^-$, $N((R_3)_2 R_4)_3^+ X^-$ or a nitrogen-containing radical,

in which

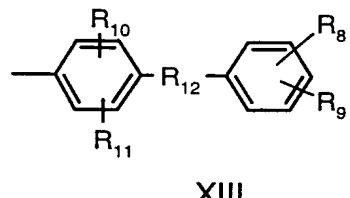
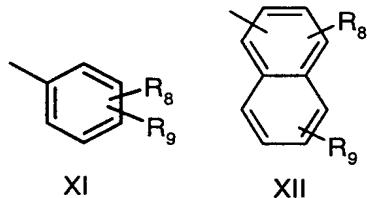
R₃ and R₄ independently of one another are hydrogen, C₁-C₁₈alkyl, C₅-C₆cycloalkyl or unsubstituted or R₇-substituted phenyl,

M is a cation of an alkali metal, preferably sodium or potassium,

X⁻ is a halide, such as fluoride, chloride, bromide or iodide, and

R₇ is hydrogen, halogen such as F, Cl, Br, I or is C₁-C₈alkyl or unsubstituted or NR₃R₄-substituted C₅-C₆cycloalkyl.

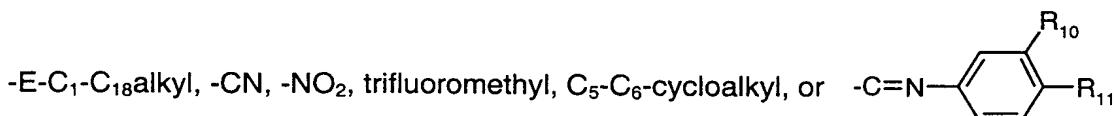
4. A process according to claim 1, wherein G₂ in halo-DPP of the formula IIa is an unsubstituted or substituted, halogenated phenyl group and G₃ is G₂ or G₁, or G₆ in halo-DPP of the formula IIb is G₁, in which
 G₁ is a heterocyclic radical or a carbocyclic group of the formulae XI, XII, XIII



in which

R₈, R₉, R₁₀ and R₁₁

independently of one another are hydrogen, halogen such as F, Cl, Br or I or C₁-C₁₈alkyl,

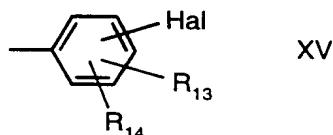


in which

E is -O-, -S-, -NH-, -C(O)O-, -OC(O)-, -(CO)NH-, -NHC(O)-, and

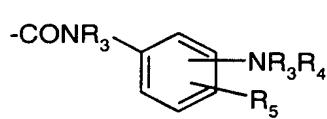
R₁₂ is a single-bond, -CH₂-, -CH(CH₃)-, -C(CH₃)₂-, -CH=N-, -N=N-, -O-, -S-, -SO-, -SO₂- or -NR₃-.

5. A process according to claim 1 or 4, wherein G₂ is a compound of the formula XV

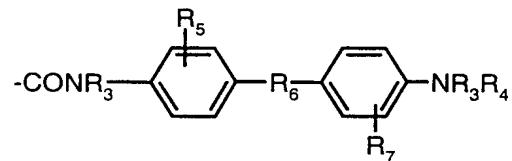


in which Hal is fluorine, chlorine, bromine or iodine and

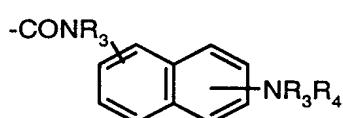
R_{13} and R_{14} independently of one another are, for example, hydrogen, CN, CF_3 , C_1 - C_5 alkyl, C_5 - C_6 cycloalkyl, -E- C_1 - C_{18} alkyl, phenyl, S- R_1 , amides, such as -CONR₃R₄ or amides of the formulae XVI to XIX



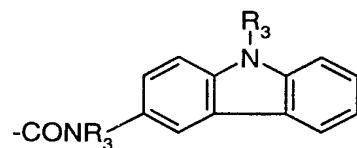
XVI



XVII



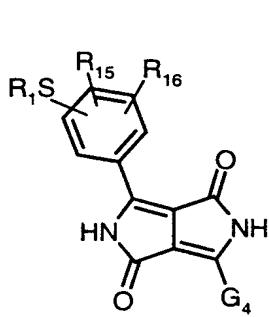
XVIII



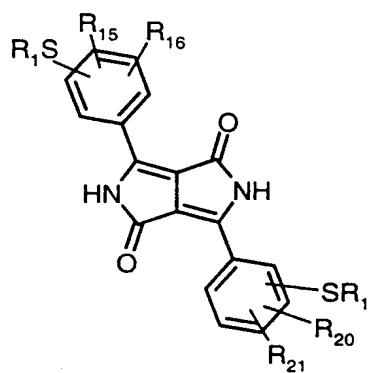
XIX

or amides of nitrogen-containing heterocycles such as 1-carbonyl-imidazole, -pyrazole, -triazole, -pyrrole, -pyrrolidine, -benzimidazole or -benzoatriazole, or halogen such as fluorine, chlorine, bromine or iodine.

6. A process according to one of claims 1 to 5, wherein the reaction is conducted in the presence of a base.
7. A process according to one of claims 1 to 6, wherein the reaction is conducted in the presence of a solvent.
8. An alkylthio- and/or arylthio-substituted diketo-diaryl-pyrrolopyrrole (DPP) of the formula XXI or XXX

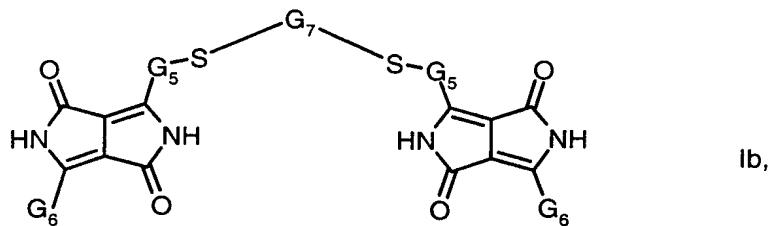


XXI



XXX

or a bis-DPP of the formula Ib



in which R₁₅, R₁₆, R₂₀ and R₂₁ independently of one another are hydrogen or R₁₃ or R₁₄, and

G₄ is a carbocyclic or heterocyclic radical, with the proviso that (a) R₁ in formula XXI is not phenyl if R₁₅ and R₁₆ are hydrogen and G₄ is phenyl, and (b) R₁ in formula XXX is not phenylene(C₁-C₄alkyl) or C₁-C₁₂alkyl if R₁₅, R₁₆, R₂₀ and R₂₁ are hydrogen, and

G₅ is a phenylene, G₆ is a carbocyclic or heterocyclic radical, and G₇ is alkylene, cycloalkylene or phenylene.

9. A composition comprising a DPP of the formula XXI and/or XXX according to claim 8 and DPP Ia and/or Ib and diketo-diaryl-pyrrolopyrrole (DPP) or a DPP latent pigment, wherein DPPs of formula XXI and Ia, or XXX and Ib are different.
10. A composition comprising a DPP of the formula XXI or XXX or bis-DPP of the formula Ib according to claim 8 and a high molecular mass organic material.
11. The use of a DPP of the formula Ia or bis-DPP of the formula Ib prepared according to claim 1 as a rheology enhancer.
12. The use of a DPP of the formula Ia or bis-DPP of the formula Ib prepared according to claim 1 as a crystal growth inhibitor.
13. The use of a DPP of the formula XXI or XXX or bis-DPP of the formula Ib according to claim 8, or of a composition according to claim 9 for colouring/pigmenting high molecular mass organic material.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 99/02513

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07D487/04 C07D519/00 A61K31/40 C07B45/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07D A61K C07B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 579 949 A (ROCHAT ALAIN C ET AL) 1 April 1986 (1986-04-01) cited in the application column 2, line 55 - line 59; claim 1; example 1 ---	1,8-13
A	EP 0 184 982 A (CIBA GEIGY AG) 18 June 1986 (1986-06-18) claims 1,8; example 4 ---	1,8-13
A	EP 0 187 620 A (CIBA GEIGY AG) 16 July 1986 (1986-07-16) example 6 -----	1,8-13

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

8 September 1999

20/09/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Bosma, P

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 99/02513

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US 4579949	A 01-04-1986	AT 22104	T	15-09-1986
		AU 568298	B	24-12-1987
		AU 1444783	A	24-11-1983
		BR 8302570	A	17-01-1984
		CA 1236105	A	03-05-1988
		CS 236794	B	15-05-1985
		DD 209832	A	23-05-1984
		DK 217683	A, B,	18-11-1983
		EP 0094911	A	23-11-1983
		JP 1746176	C	25-03-1993
		JP 4025273	B	30-04-1992
		JP 58210084	A	07-12-1983
		SU 1225489	A	15-04-1986
		ZA 8303468	A	29-02-1984
EP 0184982	A 18-06-1986	CA 1260476	A	26-09-1989
		JP 1983582	C	25-10-1995
		JP 7021122	B	08-03-1995
		JP 61115960	A	03-06-1986
		US 4778899	A	18-10-1988
		US 4659775	A	21-04-1987
EP 0187620	A 16-07-1986	CA 1322758	A	05-10-1993
		JP 1902105	C	08-02-1995
		JP 6019040	B	16-03-1994
		JP 61162555	A	23-07-1986
		US 4632893	A	30-12-1986
		US 4760151	A	26-07-1988